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(54) A DEVICE FOR MEASURING THE OXYGEN IN A METAL BATH

(71) We, ELECTRO-NITE N.V., of Grote Baan 27a, Houthalen, Belgium, a Belgian Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to devices for measuring the oxygen in a molten metal bath, especially in a molten iron or molten steel bath, by an electrochemical method.

The steelmaker has a notable interest in obtaining in the shortest possible time precise information relative to the oxygen content of a metal bath, and especially an iron bath during refining.

This information is usually supplied by measuring probes based on electrochemical processes, which, by measuring potential difference between two suitable electrodes immersed in the bath, enable its oxygen activity to be determined.

Generally one of the electrodes of these probes is of an elongated small-diameter cup shape, and the other is in the form of a metal rod.

Numerous types of such probes have already been proposed, and they usually comprise a first electrode placed at the bottom of a quartz or refractory tube sealed (at the end to be immersed in the bath) by a refractory oxide pellet, the oxide being an ionic conductor,

a layer of powder material placed in the bottom of the tube and adapted to give good contact between the end of the electrode and the inner face of the pellet, this material developing a definite partial pressure of oxygen, a second electrode, consisting for example of a metal (e.g. iron) rod, a thermocouple for measuring the bath temperature.

In order to simplify both the manufacture of the probes and their manipulation, these electrodes are usually combined in a single measuring cell which, with its support, forms a probe which is very easy to handle

and of which the various pieces are interchangeable because of standardisation of their shapes and dimensions.

The operation of known devices for measuring oxygen activity is sometimes disturbed by special factors which, in certain cases, can lead to deterioration of these devices.

In this respect, internal overpressure has been found to arise in these devices due to the action of temperature, notably on the water of crystallisation contained in the refractory, on the air in the powder pores, and on the organic materials which, whatever precautions are taken, are practically always found in small concentrations in the refractory cement plugs used for fixing together the various constituent members of the cell. Because of the temperature, the organic materials at least partially decompose and are subjected to at least partial combustion, the water of crystallisation evaporates and the air expands, these three factors creating an internal gaseous pressure which either originates in the quartz tube or spreads there and causes loosening or even expulsion of the refractory oxide pellet set in the end of the quartz tube, particularly where, owing to the temperature, the quartz tube is in its softening zone.

In order to remedy this disadvantage, cavities or expansion chambers designed to prevent to a certain extent the appearance of these overpressures have been arranged in the plugs, but it has been established that this practice leads to larger final dimensions for the cell head.

What is desired is a cell which possesses complete insensitivity to any possible overpressure which may originate in the interior of the cell, whatever the origin of this overpressure may be.

The present invention provides a device for measuring the oxygen activity and temperature of a bath of molten metal, comprising a probe which is to be mounted on the end of a hollow probe-supporting rod, the probe comprising: a thermocouple; an

electrically conducting first electrode; a tube closed at its end to be immersed in the molten metal, at least the said end of the tube consisting of a refractory oxide cement which is an ionic conductor; an electrically conducting second electrode, disposed in the tube; a layer of powdery material disposed in the tube and being in contact with the second electrode and the inner wall of the closed end of the tube, the powdery material comprising a metal element mixed with its oxide; a layer of refractory powdery material in the tube adjacent the first-mentioned layer of powdery material; the first electrode, the tube, and the thermocouple being disposed in such a manner that, on immersion of the probe, they are plunged into the metal bath and enter into contact with it; and an evacuation duct (preferably of metal) one end of which is located in the tube (preferably in the layer of refractory powdery material) and the other end of which projects into a free space for communication with atmospheric pressure.

The invention will be described further by way of example only, with reference to the accompanying drawing, whose sole Figure is a longitudinal section through the extremity of a probe for measuring the oxygen activity and temperature of a bath of molten metal.

This probe extremity comprises an external casing 1 consisting of a cylindrical tube of a refractory material. This casing 1 surrounds and protects a cardboard tube 2, covered at its end with a refractory sleeve 3 filled and closed by a refractory cement plug 4.

The exposed end of the plug 4 is surrounded by a metal cylinder 5 which forms a first electrode, whose projecting end 6 is to come into contact with the metal bath; it rigidly holds a U-tube 7 containing a thermocouple for measuring the bath temperature, and a quartz tube 8 whose lower end is filled by a solid electrolyte 9, for example zirconia. (Alternatively, the whole of the tube 8 and electrolyte 9 would be integrally formed and consist of a refractory oxide cement.) In the tube 8 there is a second electrode 10 which, together with the electrode 6, enables the electromotive force deriving from the oxygen activity of the metal bath to be measured. The end of this electrode is surrounded by a powder 11 (for example of $\text{Cr} - \text{Cr}_2\text{O}_3$) which favours electrical contact between the electrode 10 and solid electrolyte 9, and which develops a given partial pressure of oxygen. Above the powder 11 the quartz tube 8 is filled with a powder 12 which is a powdery refractory and electrically insulating material, for example powdered alumina.

Formed in this manner, the probe is mounted by friction on a probe support rod

21, which is hollow and contains the electrical connectors (not shown) which connect to conductors 13, 14, and 15 (connected to the electrodes and thermocouple) whose terminals are shown very diagrammatically in the drawing, and which allow measurement of the temperature T (conductors 13, 14) and measurement of the electromotive force E (conductors 13, 15).

Protection against any possible internal overpressure is obtained by means of a hollow duct 16, for example of metal (e.g. steel or copper) one end 17 of which is in the quartz tube 8, preferably in the zone occupied by the powder 12, and the other end 18 of which projects into the interior of the tube 2 through a hole 19 in a plate 20 which internally caps the plug 4 and sleeve 3. Moreover, this end 18 is located in the hollow interior of the probe support rod 21 (whose end is shown diagrammatically). Any overpressure material, gaseous or otherwise, appearing for example in the plug 4 and spreading into the quartz tube or appearing in the tube itself, easily escapes through the duct 16, the end 18 of which is practically in free air.

On immersion of the probe, the electrode 6, the end of the tube 8, and the thermocouple 7 are plunged into the metal bath and enter into contact with it.

WHAT WE CLAIM IS:—

1. A device for measuring the oxygen activity and temperature of a bath of molten metal, comprising a probe which is to be mounted on the end of a hollow probe-supporting rod, the probe comprising: a thermocouple; an electrically conducting first electrode; a tube closed at its end to be immersed in the molten metal, at least the said end of the tube consisting of a refractory oxide cement which is an ionic conductor; an electrically conducting second electrode, disposed in the tube; a layer of powdery material disposed in the tube and being in contact with the second electrode and the inner wall of the closed end of the tube, the powdery material comprising a metal element mixed with its oxide; a layer of refractory powdery material in the tube adjacent the first-mentioned layer of powdery material; the first electrode, the tube, and the thermocouple being disposed in such a manner that, on immersion of the probe, they are plunged into the metal bath and enter into contact with it; and an evacuation duct one end of which is located in the tube and the other end of which projects into a free space for communication with atmospheric pressure.

2. A device as claimed in claim 1, in which the tube consists wholly of the said cement.

3. A device as claimed in claim 1 or 2, 130

in which the refractory powdery material is electrically insulating.

4. A device as claimed in claim 3, in which the refractory powdery material is powdered alumina.

5. A device as claimed in any of claims 1 to 4, in which the said one end of the evacuation duct is located in the refractory powdery material.

10 6. A device as claimed in any of claims 1 to 5, in which the evacuation duct is of metal.

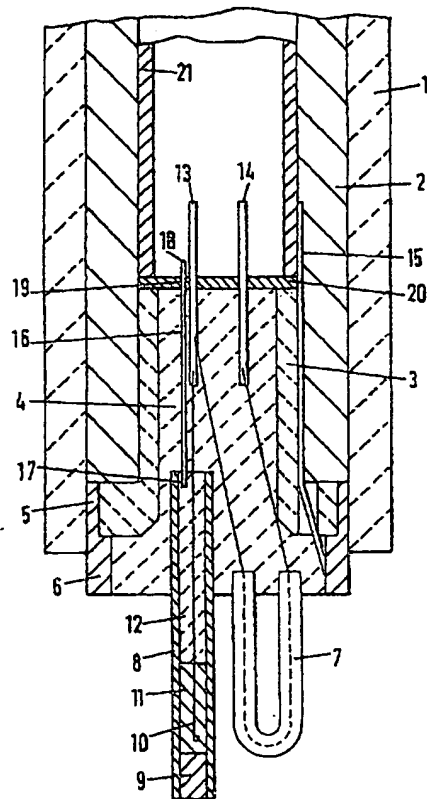
7. A device for measuring the oxygen activity and temperature of a metal bath, substantially as described herein with reference to and as shown in the accompanying drawing. 15

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1473761 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of
the Original on a reduced scale*



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